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Quenching Rate Constants and Product Assignments for Reactions of Xe(7p[3/2]$_2$, 7p[5/2]$_2$ and 6p'[3/2]$_2$) Atoms with Rare Gases, CO, H_2, N_2O, CH_4 and Halogen-Containing Molecules

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For constant laser power and bandwidth, the two-photon cross-section is proportional to the square of the two-photon matrix element, $M_{f,g}$.

$$M_{f,g} = \frac{2\pi}{h} \sum_k \frac{\mu_{kf}\mu_{gk}}{(\omega_{gk}-\omega_L)} \qquad (5a)$$

If the integrals are assumed to be positive, the individual dipole matrix elements in Eq. (5a) can be expressed in terms of the oscillator strengths of the corresponding spectral lines. For linear polarization of the laser beam, only transitions to Xe* substates with $m_J=0$ are allowed and Eq. 5b can be used.

$$M_{f,g} = \frac{2\pi}{h} \sum_k \frac{G_{g,k,f}}{(\omega_{gk}-\omega_L)} \left[\frac{f_{kf}f_{gk}}{(\omega_{gk}X\omega_{kf})}\right]^{1/2} <J_f 100|10><1100|00> \qquad (5b)$$

$G_{g,k,f}$ is a factor depending upon the degeneracy of atomic states and the last two terms in brackets are the Clebsh-Gordon coefficients. If the intermediate state, k, lies below the final state, $G_{g,k,f}=g_g/g_f$, if state k is above the final state, $G_{g,k,f}=g_g^2/g_k g_f$. The results of the calculations are presented in Table 7. The 6s[3/2]$_1$ intermediate state is the most important for the Xe(6p) cross section; but, several intermediate states could contribute to the Xe(6p',7p) cross sections. The calculated relative two-photon cross-sections for all Xe(6p,7p,6p') states are of the same order of magnitude, assuming that all the individual matrix elements are positive. In general, the oscillator strengths for s->p transitions are more accurate than for d->p transitions; the reliability could be particularly poor for nd(J=1) → np(J=0) transitions, since these levels are very sensitive to configuration mixing[20a]. The uncertainty of the matrix element for the 7p[1/2]$_0$ state could be especially large due to contributions from routes involving the nd(J=1) states to the total value of $M_{f,g}$ and to the contribution from several intermediate states. Indeed, this state reveals the largest disagreement with the experimental value. Since the calculated two-photon matrix elements generally agree with the experimental data for the 6p and 6p' states, the contributions of individual intermediate states to the sum apparently do not cancel.

H-S 180-2.

Table 7. Two-photon matrix elements[a], $M_{f,g}$, for transitions to 6p, 6p′ and 7p states of Xe

Final State	$6p[1/2]_0$	$6p[3/2]_2$	$6p[5/2]_2$	$6p'[1/2]_0$	$6p'[3/2]_2$	$7p[1/2]_0$	$7p[3/2]_2$	$7p[5/2]_2$
Intermediate State								
$6s[3/2]_1$	100[a]	74	109	14	12	20	11	10
$7s[3/2]_1$	21	36	45	32	0	73	72	94
$6s'[1/2]_1$	26	31	1	49	83	26	17	19
$7s'[1/2]_1$	0	0	0	13	38	6	9	8
$5d[1/2]_1$	3	7	4	9	13	6	3	4
$6d[1/2]_1$	1	2	1	1	2	3	5	4
$7d[1/2]_1$	2	3	1	6	2	1	10	7
$5d[3/2]_1$	75	5	27	30	12	34	3	10
$6d[3/2]_1$	18	0	4	28	4	66	3	27
$7d[3/2]_1$	1	0	0	1	1	1	1	1
$5d'[3/2]_1$	3	1	1	3	12	21	3	4
$6d'[3/2]_1$	1	0	0	11	4	5	1	0
$7d'[3/2]_1$	0	0	0	4	1	3	0	1
$\lvert\Sigma M_{f,g}\rvert^2$ [b]	2.4	1.0	1.5	1.6	1.3	2.7	0.7	1.4
experimental	2-3	1.0	1.6-2.0	1.2	1.0	0.25	0.7	0.3
cross sections[c,d]				1.6	1.3	0.3	0.9	0.4

a. For convenience of presentation, the individual matrix elements are given as relative values with the transition to the $6p[1/2]_0$ via $6s[3/2]_1$ set equal to 100. The oscillator strengths from the ground state were taken from references 20d; the oscillator strengths for the transitions from the ns and nd resonance states to the final np states were taken from ref. 21 or 20c.

b. The total relative excitation cross section, which is the square of the sum over the $M_{f,g}$ values, is presented relative to $6p[3/2]_2$ state as 1.0.

c. See text for the description of the experimental values for Xe(6p) states.

d. See text for the experimental Xe(6p′,7p) values. The experimental comparison of $6p[3/2]_2$ and $6p'[3/2]_2$ cross sections gave a ratio of unity; however, the uncertainty is large and the second line shows the experimental results if the $6p'[1/2]_0$ relative cross section is scaled to the calculated value.